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**Mass spectral data of trimethylsilyl esters of
alkyl and cycloalkyl methylphosphonates**

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Mass spectral data of trimethylsilyl esters of alkyl and cycloalkyl methylphosphonates

Ir. E.R.J. Wils, Ing. A.L. de Jong
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mei 1999

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Probleemstelling

In opdracht van het Ministerie van Defensie doet het TNO Prins Maurits Laboratorium (TNO-PML) al sinds de jaren zeventig onderzoek naar monsternamen en identificatie van chemische strijdmiddelen.

Chemische strijdmiddelen kunnen geïdentificeerd worden aan de hand van hun spectrum. Een spectrum kan worden beschouwd als een vingerafdruk van een chemische verbinding. In NATO-verband is een database opgebouwd met spectra van verschillende bekende chemische strijdmiddelen. Identificatie van onbekende middelen kost echter veel tijd, zelfs als de verwantschap met een bestaande verbinding erg groot is. Bovendien zal er altijd behoefte zijn de identificatie te toetsen door de verbinding ook zelf samen te stellen (synthetiseren) en het spectrum daarvan, vergelijkend, te meten.

Het onderhavige rapport beschrijft het onderzoek naar een methode die de identificatie van chemische strijdmiddelen aanzienlijk versnelt.

Beschrijving van de werkzaamheden

Sarin-homologen zijn bekende chemische strijdmiddelen, gevormd uit alcoholen en fosforbevattende stoffen. In eerdere studies zijn op het TNO-PML ongeveer zestig alcoholen als mogelijke synthese-kandidaten voor sarin-homologen geselecteerd. Van deze gesynthetiseerde sarin-homologen zijn de spectra bepaald. Er is bovendien een methode ontwikkeld die het mogelijk maakt binnen een uur over het spectrum te beschikken.

De sarin-homologen zijn niet stabiel in het milieu en zullen na verloop van enkele uren tot dagen in de grond, en zeker in water, ontleden naar de alkyl en cycloalkyl methyl-

fosfonzuren. Deze alkyl en cycloalkyl methylfosfonzuren zijn ook primaire afbraakproducten van V-strijdmiddelen (bijvoorbeeld VX). De alkyl en cycloalkyl methylfosfonzuren kunnen niet als zodanig bepaald worden en moeten omgezet worden in overeenkomstige vluchtige verbindingen. Omzetting tot de trimethylsilyl (TMS-) esters is daarbij een van de meest toegepaste methodes. Spectra van de ontledingsproducten van de bekende chemische strijdmiddelen sarin, soman en cyclohexylsarin zijn in het verleden al opgenomen. Er ontbreken echter nog spectra van andere TMS-esters van ontledingsproducten van sarin-homologen. Bovendien bestaat er behoefte aan methodes om deze snel, op kleine schaal, te kunnen synthetiseren.

Op basis van de eerder ontwikkelde procedure voor de synthese van sarin-homologen is een soortgelijke procedure voor synthese van de TMS-esters van de corresponderende zuren succesvol ontwikkeld.

Resultaten en vervolgonderzoek

Het is nu mogelijk om binnen enkele uren over het spectrum van een TMS-ester van een ontledingsproduct van een sarin-homoloog te beschikken. De gevonden spectra worden in een bestand opgenomen.

Ook voor andere strijdmiddelen, of ontledingsproducten daarvan, is het nuttig om vergelijkbare methodes te ontwikkelen.



Projectinformatie

Projecttitel

Identificatie van chemische strijdmiddelen

Projectnummer TNO-PML

014.11024

Omschrijving programma

Voor 1999 is het volgende programma afgesproken.

- Afronden van het onderzoek naar de analyse van tetanustoxine.
- Starten van het onderzoek aan ricine en nagaan van een eventuele samenwerking met CBDS, Porton Down op dit gebied.
- Deelname aan een ringonderzoek in het kader van de NATO/SIBCA-groep betreffende de analyse van 'mid-spectrum agents' (toxinen).
- Uitbreiden van het TNO-PML databestand met spectra van TMS-gederivatiseerde alkylfosfonzuren (hydrolyseproducten van zenuwgassen).

Activiteiten in verband met de NATO/SIBCA-groep (onder andere samenstellen SIBCA-Handboek, deelname vergaderingen).

Planning programma (tijdspad)

Projectbegeleider defensie

G.M. Swenker, LBBKL-PGU/GVG.

Projectleider TNO-PML

ir. E.R.J. Wils, Divisie Toxische Stoffen, Groep Analyse Toxische en Explosieve Stoffen.

Communicatie

Er is overleg gepleegd over dit onderdeel van het programma.



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Annex

A EI Mass spectral data

1 Introduction

The recording of reference spectra has always been an important aspect of the assignment 'Sampling and Identification of Chemical Warfare Agents' (A93KL424), which the TNO Prins Maurits Laboratory (TNO-PML) has performed for the Netherlands Ministry of Defence since the beginning of the 1970s. Chemical warfare (CW) agents and their decomposition products can be identified readily when a compilation of spectra is available. In Volume III of the NATO/SIBCA AEP-10 Handbook, spectral data of several hundreds of chemicals of CW interest is presented [1]. Experience has shown that the identification of an unknown, even if there is a relation with known chemicals, may take a significant amount of time. Moreover, there will always be the need to verify the identification by synthesis of the compound and the subsequent recording of its spectral data. Alkyl and cycloalkyl methylphosphonofluoridates constitute a series of chemicals to which belong the well-known CW agents sarin (GB, alkyl: isopropyl), soman (GD, alkyl: pinacolyl) and cyclohexylsarin (GF). The alkyl and cycloalkyl methylphosphonofluoridates are mentioned in the Chemical Weapons Convention under the Schedule 1 chemicals [2]. In principle, several commercial alcohols can be used for the preparation of these sarin homologues with methylphosphonic difluoride. In an earlier study by TNO-PML, approximately 60 alcohols were selected as possible candidates [3]; these were only primary and secondary alcohols, which were also relatively inexpensive. Electron impact (EI) mass spectra of the more than 60 synthesised alkyl and cycloalkyl methylphosphonofluoridates were recorded by means of gas chromatography-mass spectrometry (GC-MS). Because synthesis of the sarin homologues is time consuming and costly, the chemicals were prepared *in situ* on a small scale, by mixing the precursor methylphosphonic difluoride with a selected alcohol in methylene dichloride solvent, and were subsequently analysed by GC-MS of the reaction mixture. In this way, a reference mass spectrum could be produced within one hour. Sarin homologues, and also V-agents, are not stable in the environment and will decompose in due course on soil, and particularly in water, to the polar alkyl and cycloalkyl methylphosphonates. Although a procedure based on the combination of liquid chromatography-mass spectrometry (LC-MS) is the favoured approach for the identification of these primary decomposition products, EI mass spectra are still needed to support the LC-MS analysis results. The alkyl and cycloalkyl methylphosphonates can only be analysed by GC-MS after derivatisation to more volatile esters. Conversion to a trimethylsilyl (TMS) ester is one of the most applied derivatisation procedures. It has not only been used widely in general GC based analysis of alkyl and cycloalkyl methylphosphonates [4-6], but also in forensic toxicology studies after the Japanese sarin and VX attacks [7-11]. In addition, EI mass spectra of the TMS derivatised decomposition products of the well-known CW agents sarin and soman have been recorded in the past and taken up in Volume III of the AEP-10 Handbook. These sources are limited to spectra of frequently occurring agents, such as sarin, soman, and VX. However, spectra of the

TMS esters of other alkyl and cycloalkyl methylphosphonates were still lacking. Moreover, there was a need to produce these derivatives rapidly and on a small scale. Based on the earlier developed procedure for the preparation of sarin homologues [3], the development of a similar procedure for the TMS esters was investigated and is reported here.

2 Experimental part

2.1 Preparation of the TMS esters

Approximately 200 mg of methylphosphonic difluoride (prepared at TNO-PML) was dissolved in 4 ml of acetonitrile (Merck, p.a.). From this solution, 0.1 ml was transferred into a septum capped vial (4 ml) and, subsequently, 10 μ l of an alcohol (purchased from Aldrich) was added. The solution was allowed to stand for at least 30 minutes at room temperature, during which the formation of a specific alkyl/cycloalkyl methylphosphonofluoridate took place.

The solution containing the alkyl/cycloalkyl methylphosphonofluoridate was mixed with 100 μ l demineralized water and allowed to stand for at least 30 minutes at room temperature, during which hydrolysis towards the corresponding methylphosphonate occurred. Afterwards, the contents of the vial were evaporated to dryness with a gentle nitrogen stream, at room temperature. To the residue obtained, 100 μ l of N-methyl-N-trimethylsilyl-trifluoroacetamide (MSTFA; 1% in acetonitrile) and 100 μ l acetonitrile were added, subsequently, in order to trimethylsilylate the alkyl/cycloalkyl methylphosphonate. The mixture was allowed to react at 70 °C for 30 minutes.

2.2 GC-MS analysis

After appropriate dilution of the reaction mixture (as obtained above) with acetonitrile, 0.5 μ l of the mixture was injected onto a fused silica capillary column (50 m \times 0.3 mm ID, df 0.25 μ m) coated with CPSil5CB (Chrompack), by means of a Carlo-Erba on-column injector installed on an HP 5890A gas chromatograph (Hewlett Packard). The column was directly connected to the ion source of a VG70-250S (Micromass) double-focusing mass spectrometer. The temperature of the interface was 250 °C. The helium flow rate was around 1.5 ml/min. Generally the following temperature programme was used: 90 °C (5 min.), 8 °C/min. to 275 °C (5 min.).

EI mass spectra were recorded under low resolution conditions (static resolving power approximately 1000, 10% valley) using continuous scanning over the mass range m/z 25-500 every second. The following typical EI source conditions were applied: 70 eV ionisation energy at 200 μ A emission current, 200 °C source temperature, and 5×10^{-6} mbar source pressure.

Both the mass scale and the relative intensity scale of the spectra produced were regularly checked, under the mass spectrometer quality control programme, using perfluorokerosene (PFK) and decafluorotriphenylphosphine (DFTPP), respectively. Mass spectra were background subtracted before being compiled in the TNO-PML mass spectral library, which resides on the data system of the GC-MS system.

Spectra were also converted to a PC and incorporated as user files in the TNO-PML version of the NIST (National Institute Science and Technology) Mass Spectral Library.

3 Results and discussion

3.1 Procedure

Several routes were tried to produce the TMS esters of alkyl and cycloalkyl methylphosphonates starting from methylphosphonic difluoride with a selected alcohol. The production of the alkyl/cycloalkyl methylphosphonofluoridates as the first step proceeded in acetonitrile as well as in methylene chloride [1]; acetonitrile is preferable for later hydrolysis and subsequent TMS derivatisation. Attempts to hydrolyse these sarin homologues by adding a small amount of water to the acetonitrile solution, prior to the derivatization with a silylating reagent, were not successful. Large amounts of unwanted by-products were obtained, but not the required TMS esters. Further attempts to form the TMS esters by reaction of the alkyl/cycloalkyl methylphosphonofluoridates (in acetonitrile) with the sodium salt of trimethylsilanol did not result in the desired product. In contrast, the hydrolysis of the initially formed alkyl/cycloalkyl methylphosphonofluoridates with an excess of water, and subsequent evaporation to dryness and TMS derivatization of the residue did provide useful results. A typical gas chromatogram obtained after GC/MS analysis of a reaction mixture from the latter procedure is presented in Figure 1. The main product of reaction was, generally, bis(trimethylsilyl) methylphosphonate, which is formed by replacing of the O-alkyl or -cycloalkyl group with TMS. In addition, two separate GC peaks were generally observed for the desired TMS ester; these peaks, with typical retention time difference of a few seconds, have identical mass spectra, representative of the P(+) and P(-) diastereomers. Although the TMS ester was never the main reaction product, it was formed in sufficient yield to obtain good quality mass spectra.

The overall procedure was applied using 22 alcohols: n-butanol, isobutanol, sec-butanol, n-pentanol, 2-pentanol, 3-pentanol, n-hexanol, 2-hexanol, 3-hexanol, n-heptanol, 2-heptanol, 3-heptanol, n-octanol, 2-octanol, 3-octanol, 2-ethylhexanol, n-nonanol, cyclopropylmethyl, cyclopentanol, 2-methylcyclopentanol, 3-methylcyclopentanol and cyclohexanol. EI mass spectra of the corresponding TMS esters obtained are contained in Annex A (Figures A.1-A.22). Unfortunately, no results have been obtained for n-decanol, despite the fact that the reaction time of the hydrolysis was prolonged to about a day; although the reason for this deviant behaviour is not clear, the relative hydrophobicity may play a role.

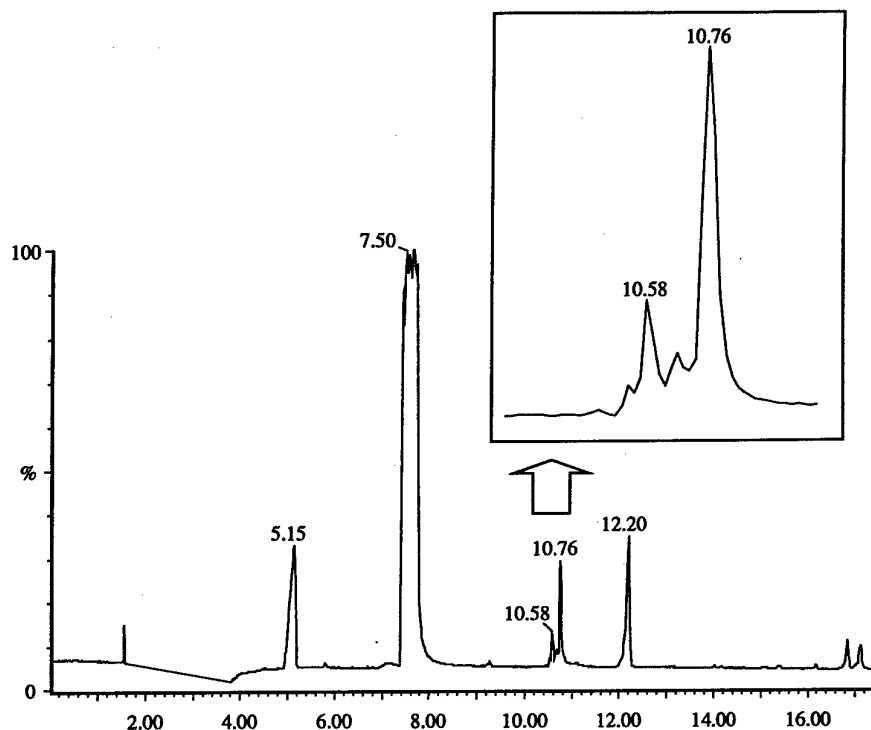


Figure 1: Total ion current chromatogram obtained after the GC/MS analysis of the reaction mixture containing (1-ethylpropyl) trimethylsilyl methylphosphonate (peak at 10.76), bis(trimethylsilyl) methylphosphonate (peak at 7.50); other peaks are from column bleeding; insert: separation of the P(+) and P(-) diastereomers of (1-ethylpropyl) trimethylsilyl methylphosphonate (without confirmed attribution of the specific diastereomer).

3.2 Mass spectra

EI mass spectra of TMS esters of some alkyl and cycloalkyl methylphosphonates have been described in the literature [5-11]. The molecular ion ($[M]^+$) is not observed in the spectra, and $[M-CH_3]^+$ is frequently present as the ion of highest mass. As a consequence, chemical ionisation will always be required for the unambiguous identification of these esters.

The fragmentation pattern for all esters studied is rather similar, because the TMS methylphosphonate part of the molecule dominates fragmentation. The base peak is invariably at m/z 153 ($[CH_3PO(OH)OSi(CH_3)_2]^+$), due to the rearrangement loss of an alkene/cycloalkene from the $[M-CH_3]^+$ ion, whereas a second abundant peak is always found at m/z 169 ($[CH_3P(OH)(OH)OSi(CH_3)_3]^+$), due to alkenyl/cycloalkenyl radical loss from the molecular ion. These m/z 153 and 169 signals are highly characteristic of the TMS alkyl/cycloalkyl methylphosphonates. Only in the spectrum of the TMS ester of cyclopropylmethyl methylphosphonate (Figure A.18) is m/z 169 of a markedly lower abundance, probably due to a characteristic competitive ethene loss (at m/z 194) from the molecular ion. The same ethene loss was

observed earlier in the EI spectrum of the corresponding cyclopropylmethyl methylphosphonofluoridate [12]. Smaller peaks at m/z 137 and 121 may be attributed to further fragmentation of m/z 169 and m/z 153, respectively. In addition, less characteristic signals from typical TMS fragment ions are present in all spectra, e.g. at m/z 73 $[\text{Si}(\text{CH}_3)_3]^+$ and m/z 75 $[\text{HOSi}(\text{CH}_3)_2]^+$. Thus, the common features of the alkyl/cycloalkyl methylphosphonate structure are easily traced in all spectra. The nature of the variant alkyl/cycloalkyl group can be derived from the signals from the alkene/cycloalkene 'molecular ion' and fragments thereof (e.g. m/z 56 and 41 for butyl), whereas the branching of the alkyl chain can in some cases be deduced through the primary neutral losses from the molecular ion. In Table 1 an overview is given of the high mass ions observed in the mass spectra of the TMS esters. The three butyl homologues, for instance, can be readily distinguished by their high mass ions. However, as the alkyl group becomes longer, the branching of the alkyl group becomes less clear from the spectrum. The esters with an alkyl chain larger than four carbon atoms show a tendency towards partial alkyl chain loss and, thus, give rise to a signal which also corresponds to the molecular ion signal of the TMS ester of ethyl methylphosphonate (at m/z 196). The high mass region of the spectra of the cycloalkyl compounds provides less information. In the mass spectra of the cyclopentyl and cyclohexyl homologues, only weak signals are present at m/z 221 and correspond to $[\text{M}-\text{CH}_3]^+$ and $[\text{M}-\text{C}_2\text{H}_5]^+$, respectively (Figures A.19 and A.22). The high mass region allows distinction between the isomeric TMS esters of 2-methyl- and 3-methylcyclopentyl methylphosphonates (Figures A.20 and A.21). Peaks are observed, inter alia, at m/z 235 ($[\text{M}-\text{CH}_3]^+$) and m/z 221 ($[\text{M}-\text{C}_2\text{H}_5]^+$) for the 2-methyl isomer, and at m/z 209 ($[\text{M}-\text{C}_3\text{H}_5]^+$) and m/z 195 ($[\text{M}-\text{C}_4\text{H}_7]^+$) for the 3-methyl isomer. This shows that identification of the variant alkyl/cycloalkyl substituent is less straightforward than that of the common TMS methylphosphonate structure.

Table 1: High mass ions in the mass spectra of the TMS esters of alkyl methylphosphonates.

| Alkyl group | MW | High mass ions (m/z) | Comments | Spectrum |
|------------------------------------|-----|---|--|------------|
| isopropyl | 210 | 195 (M-CH ₃) | | AEP-10 [1] |
| n-butyl | 224 | 209 (M-CH ₃), 195 (M-C ₂ H ₅), 181 (M-C ₃ H ₇) | | A.1 |
| 2-methylpropyl (isobutyl) | 224 | 209 (M-CH ₃), 181 (M-C ₃ H ₇) | | A.2 |
| 1-methylpropyl (sec-butyl) | 224 | 209 (M-CH ₃), 195 (M-C ₂ H ₅) | m/z 195 indicates methyl branching at position 1 | A.3 |
| pentyl | 238 | 223 (M-CH ₃), 196 (M-C ₃ H ₆), 195 (M-C ₃ H ₇) | | A.4 |
| 1-methylbutyl | 238 | 223 (M-CH ₃), 209 (M-C ₂ H ₅), 195 (M-C ₃ H ₇) | m/z 195 indicates methyl branching at position 1 | A.5 |
| 1-ethylpropyl | 238 | 223 (M-CH ₃), 209 (M-C ₂ H ₅) | m/z 209 indicates ethyl branching at position 1 | A.6 |
| hexyl | 252 | 237 (M-CH ₃), 196 (M-C ₄ H ₈), 195 (M-C ₄ H ₉) | | A.7 |
| 1-methylpentyl | 252 | 237 (M-CH ₃), 195 (M-C ₄ H ₉) | m/z 195 indicates methyl branching at position 1 | A.8 |
| 1-ethylbutyl | 252 | 223 (M-C ₂ H ₅), 209 (M-C ₃ H ₇) | m/z 209 and 223 indicate branching at position 1 | A.9 |
| 1,2,2-trimethyl-propyl (pinacolyl) | 252 | 237 (M-CH ₃), 196 (M-C ₄ H ₈), 195 (M-C ₄ H ₉) | m/z 195 and 196 point to a pinacolyl group | AEP-10 [1] |
| heptyl | 266 | 251 (M-CH ₃), 196 (M-C ₅ H ₁₀), 195 (M-C ₅ H ₁₁) | | A.10 |
| 1-methylhexyl | 266 | 251 (M-CH ₃), 195 (M-C ₅ H ₁₁) | m/z 195 indicates methyl branching at position 1 | A.11 |
| 1-ethylpentyl | 266 | 237 (M-C ₂ H ₅), 209 (M-C ₄ H ₉) | m/z 209 and 237 indicate branching at position 1 | A.12 |
| octyl | 280 | 265 (M-CH ₃), 237 (M-C ₃ H ₇), 196 (M-C ₆ H ₁₂), 195 (M-C ₆ H ₁₃) | | A.13 |
| 1-methylheptyl | 280 | 265 (M-CH ₃), 195 (M-C ₆ H ₁₃) | m/z 195 indicates methyl branching at position 1 | A.14 |
| 1-ethylhexyl | 280 | 251 (M-C ₂ H ₅), 209 (M-C ₅ H ₁₁) | m/z 209 and 251 indicate branching at position 1 | A.15 |
| 2-ethylhexyl | 280 | 251 (M-C ₂ H ₅), 223 (M-C ₄ H ₉) | m/z 223 and 251 indicate branching at position 2 | A.16 |
| nonyl | 294 | 279 (M-CH ₃), 237 (M-C ₄ H ₉), 196 (M-C ₇ H ₁₄), 195 (M-C ₇ H ₁₅) | | A.17 |

4 Conclusion and recommendation

A micro synthesis procedure has been developed for the preparation of TMS esters of alkyl and cycloalkyl methylphosphonates, the primarily degradation products of organophosphorus CW agents and similar compounds placed under Schedule 1 of the Chemical Weapons Convention. With this procedure, EI mass spectra can be recorded by GC-MS for reference purposes within a few hours. It is recommended that comparable procedures will be developed for other classes of CW agents and their degradation products, for which reference data is still lacking.

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6 Authentication



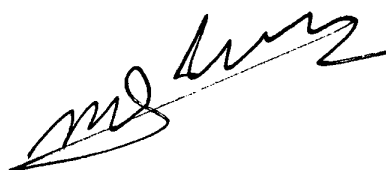
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Dr. B.L.M. van Baar
Author



Dr. M.S. Nieuwenhuizen
Group leader

Annex A EI Mass spectral data

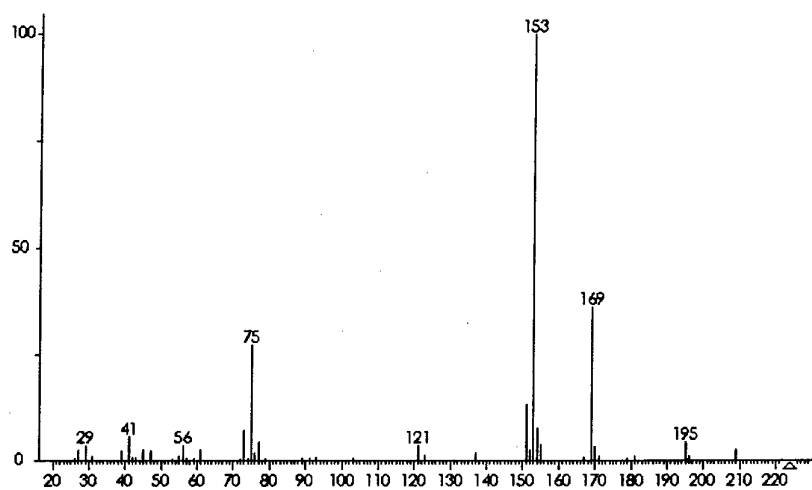


Figure A.1: Butyl trimethylsilyl methylphosphonate (MW 224).

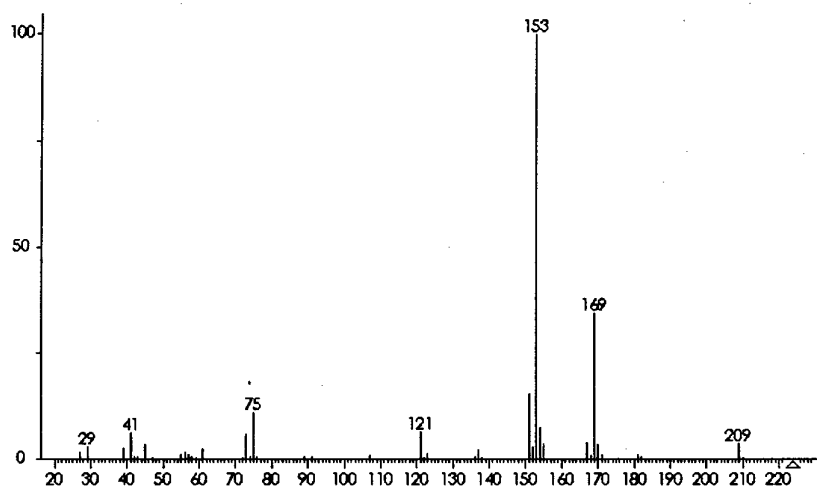


Figure A.2: Isobutyl trimethylsilyl methylphosphonate (MW 224).

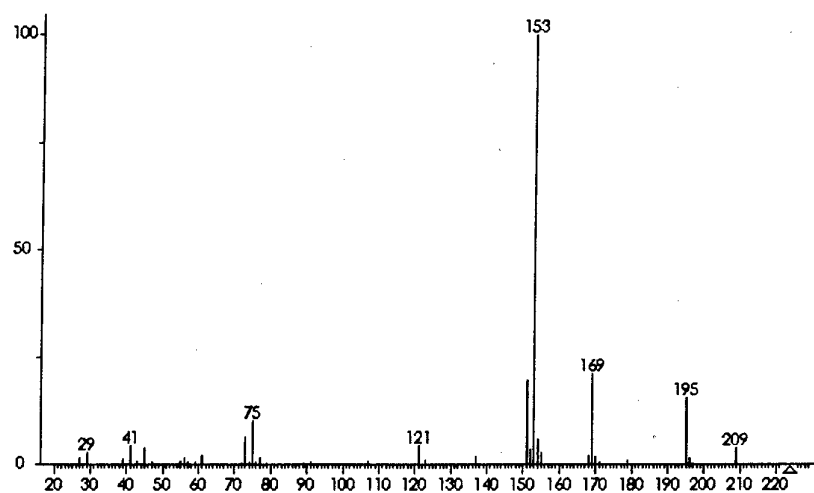


Figure A.3: *Sec-butyl trimethylsilyl methylphosphonate (MW 224).*

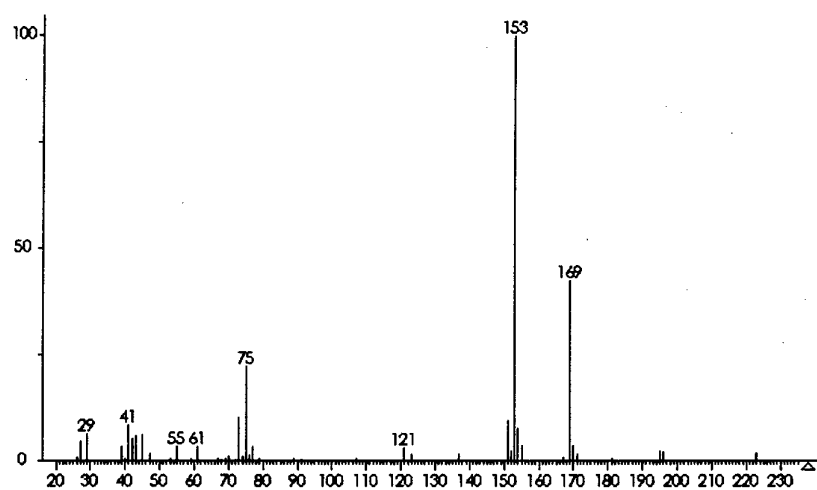


Figure A.4: *Pentyl trimethylsilyl methylphosphonate (MW 238).*

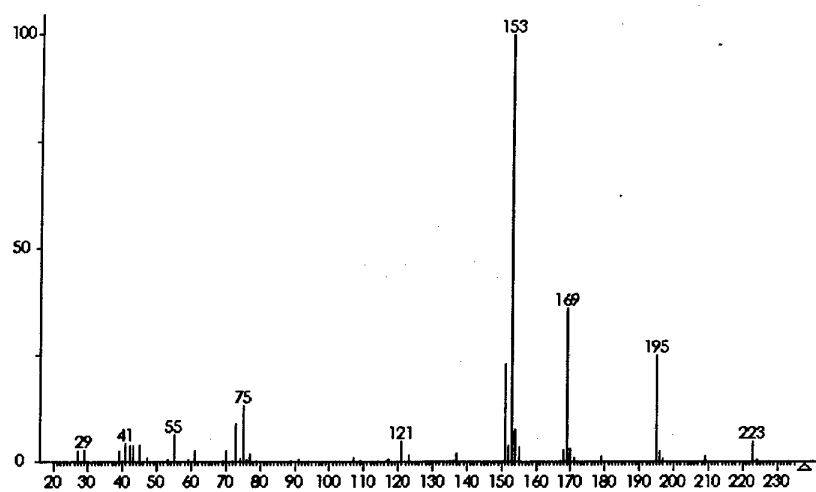


Figure A.5: *1-Methylbutyl trimethylsilyl methylphosphonate (MW 238).*

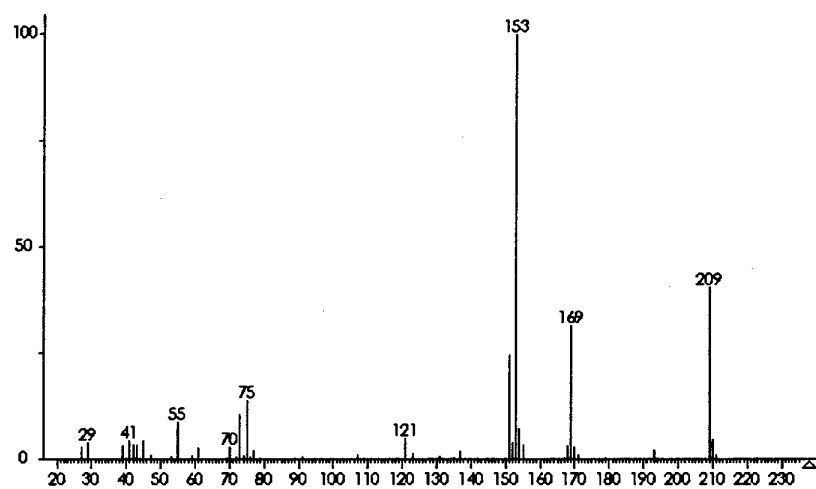


Figure A.6: *1-Ethylpropyl trimethylsilyl methylphosphonate (MW 238).*

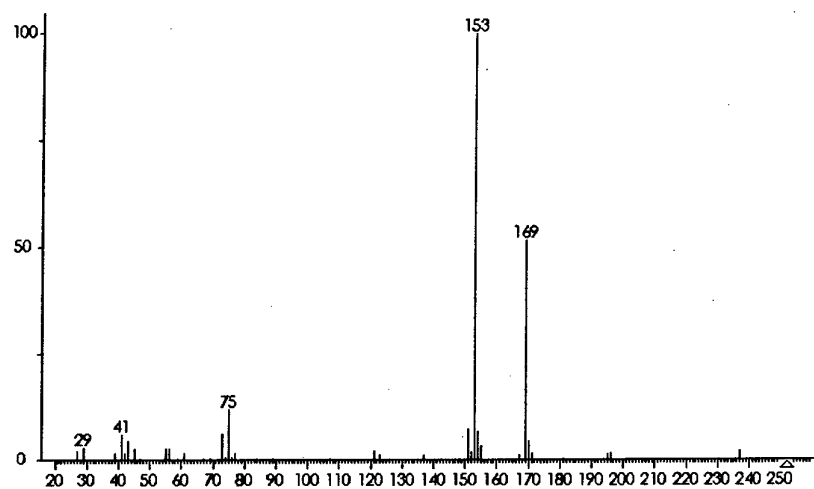


Figure A.7: Hexyl trimethylsilyl methylphosphonate (MW 252).

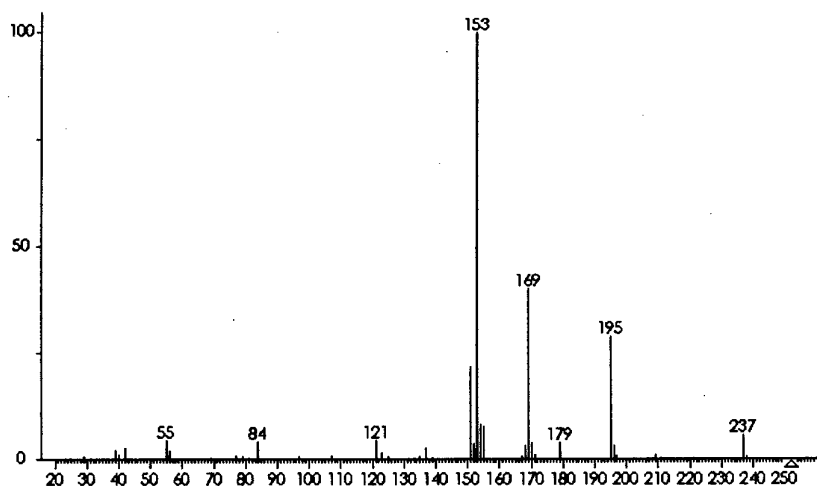


Figure A.8: 1-Methylpentyl trimethylsilyl methylphosphonate (MW 252).

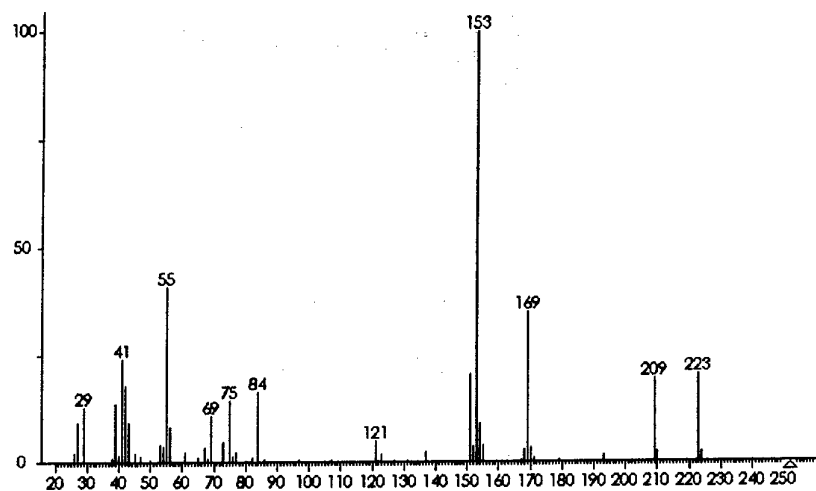


Figure A.9: 1-Ethylbutyl trimethylsilyl methylphosphonate (MW 252).

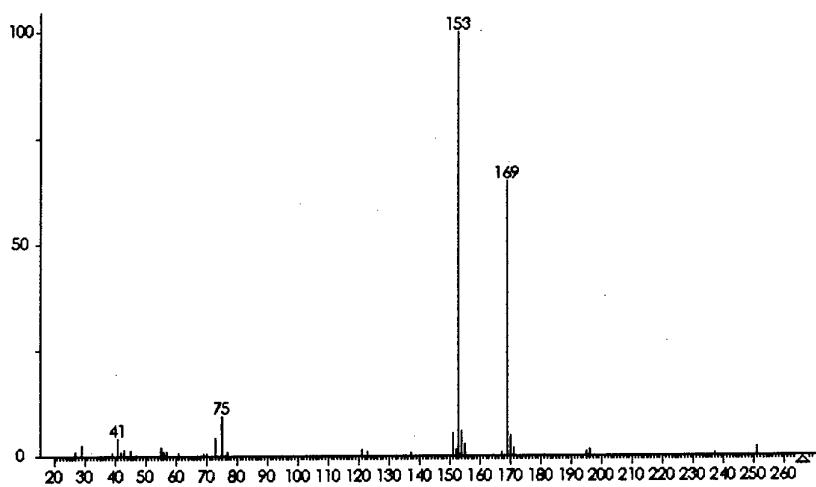


Figure A.10: Heptyl trimethylsilyl methylphosphonate (MW 266).

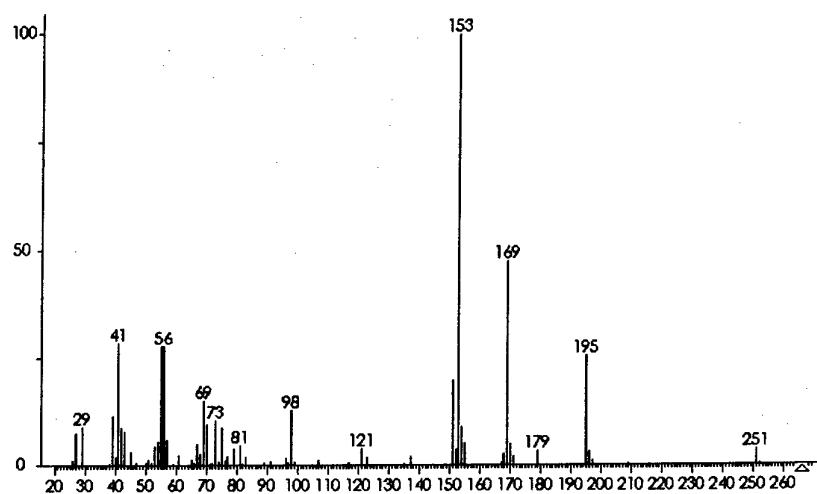


Figure A.11: 1-Methylhexyl trimethylsilyl methylphosphonate (MW 266).

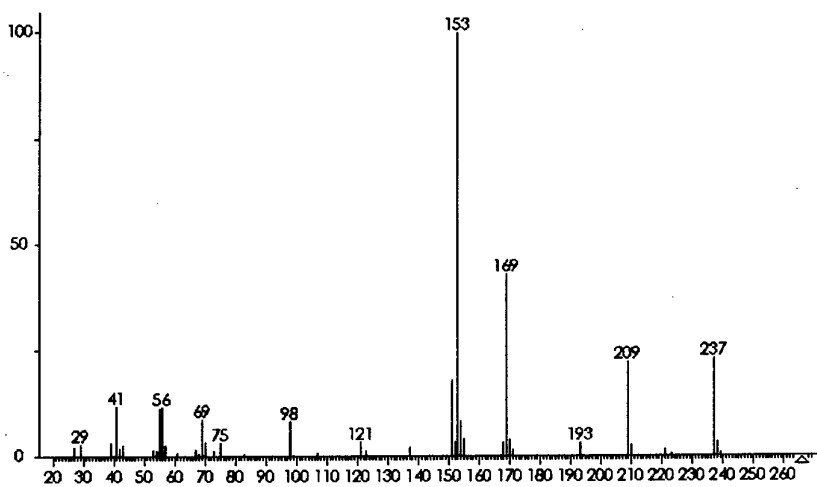


Figure A.12: 1-Ethylpentyl trimethylsilyl methylphosphonate (MW 266).

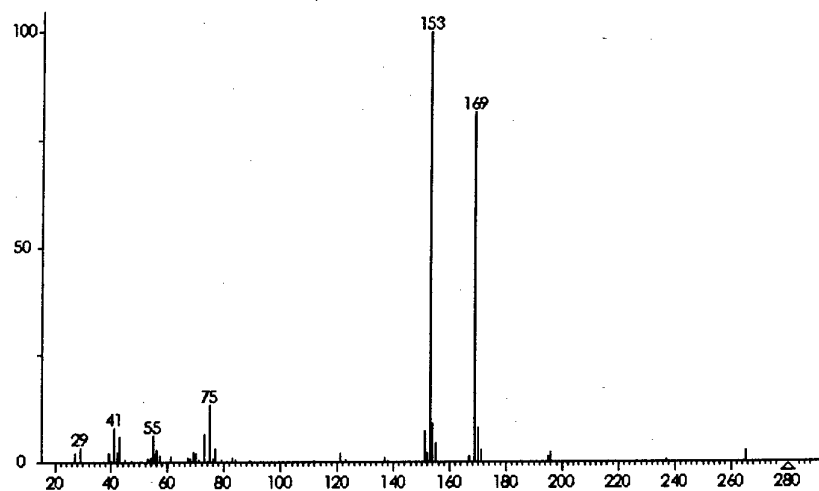


Figure A.13: Octyl trimethylsilyl methylphosphonate (MW 280).

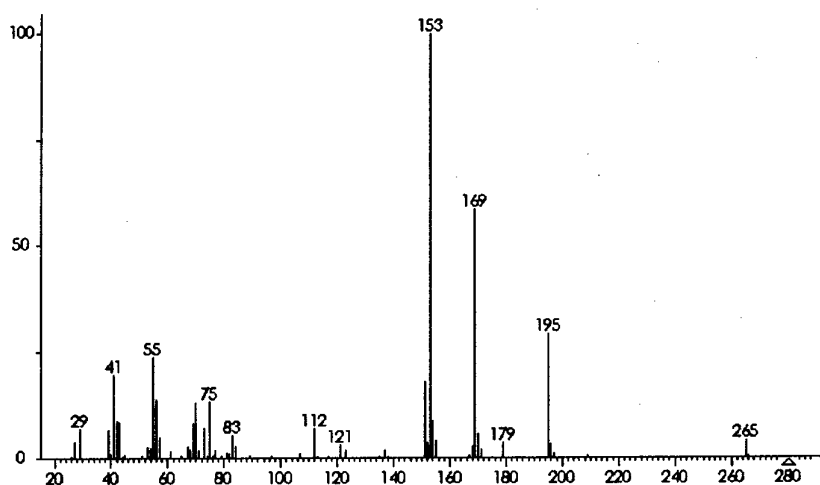


Figure A.14: 1-Methylheptyl trimethylsilyl methylphosphonate (MW 280).

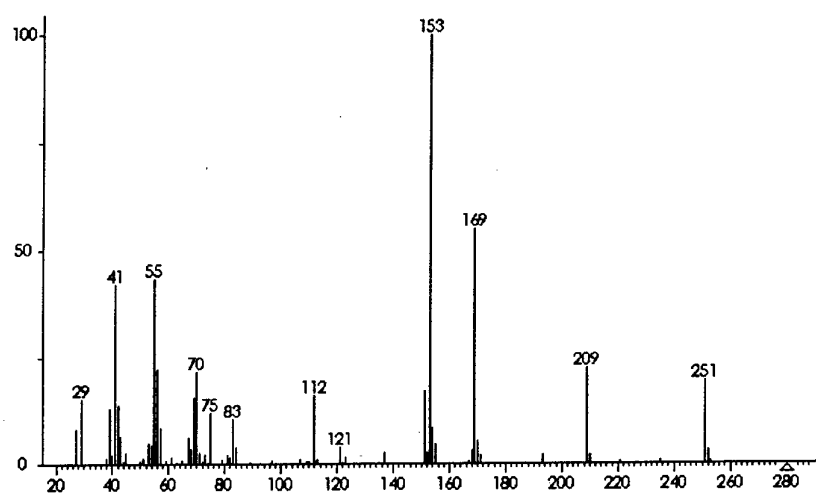


Figure A.15: 1-Ethylhexyl trimethylsilyl methylphosphonate (MW 280).

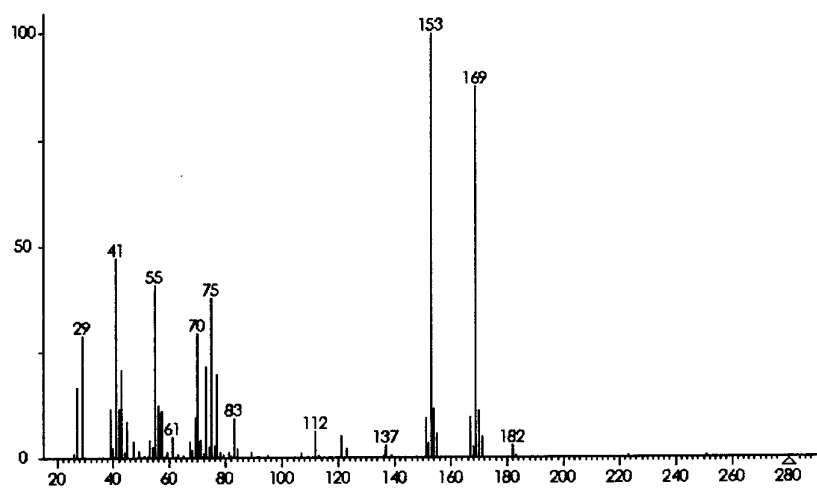


Figure A.16: 2-Ethylhexyl trimethylsilyl methylphosphonate (MW 280).

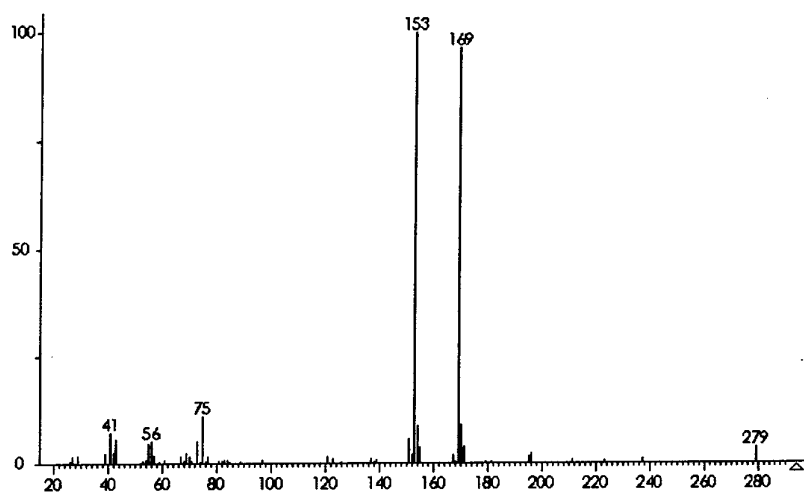


Figure A.17: Nonyl trimethylsilyl methylphosphonate (MW 294).

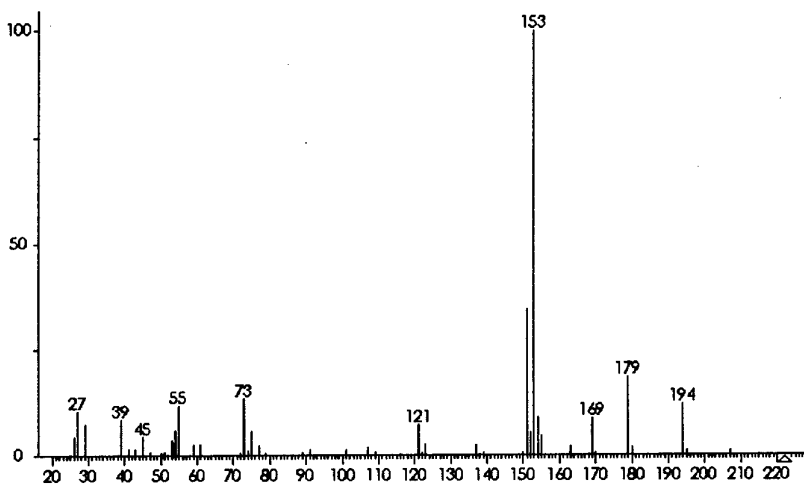


Figure A.18: Cyclopropylmethyl trimethylsilyl methylphosphonate (MW 222).

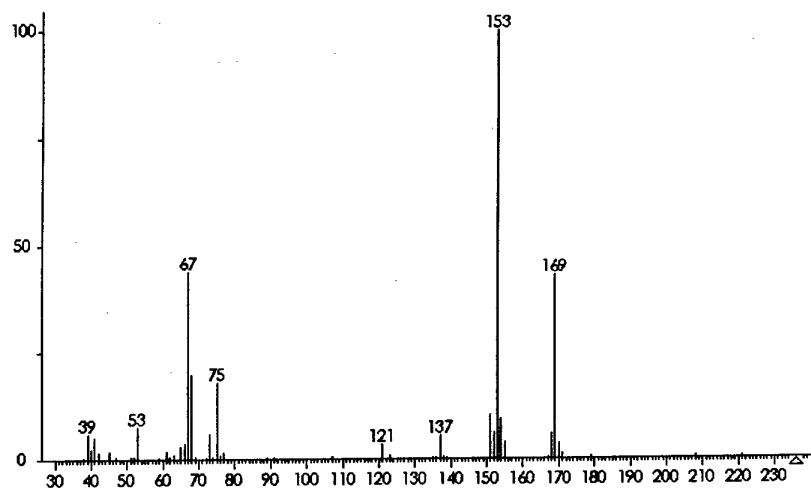


Figure A.19: Cyclopentyl trimethylsilyl methylphosphonate (MW 236).

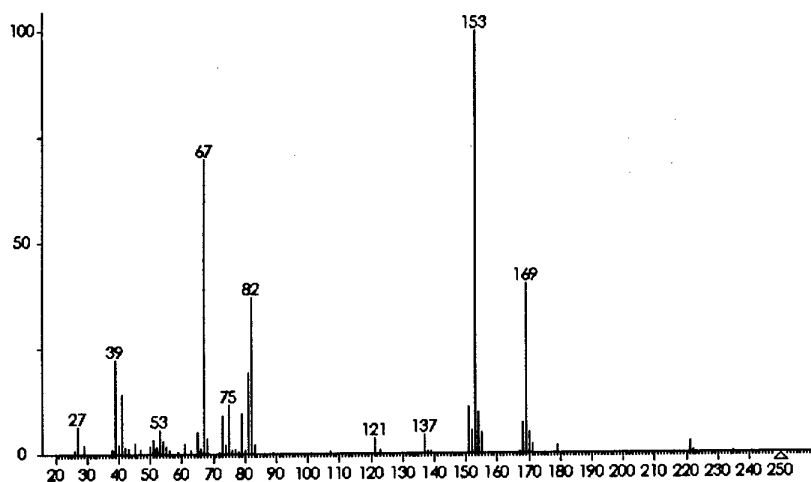


Figure A.20: 2-Methylcyclopentyl trimethylsilyl methylphosphonate (MW 250).

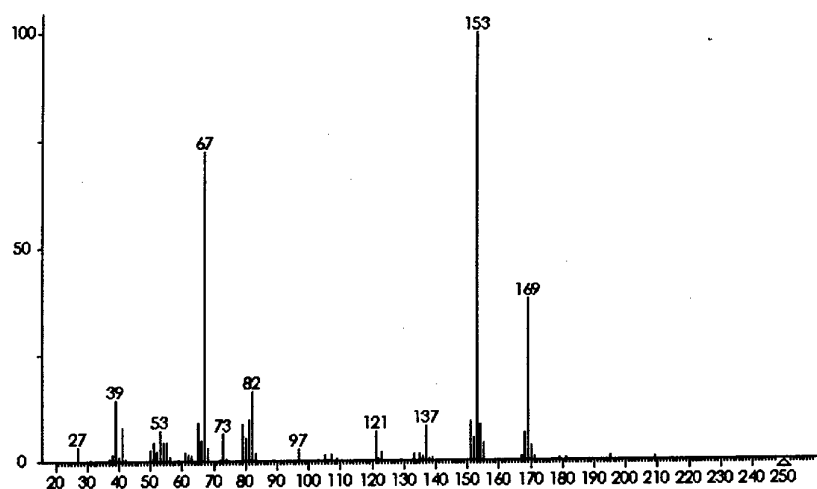


Figure A.21: 3-Methylcyclopentyl trimethylsilyl methylphosphonate (MW 250).

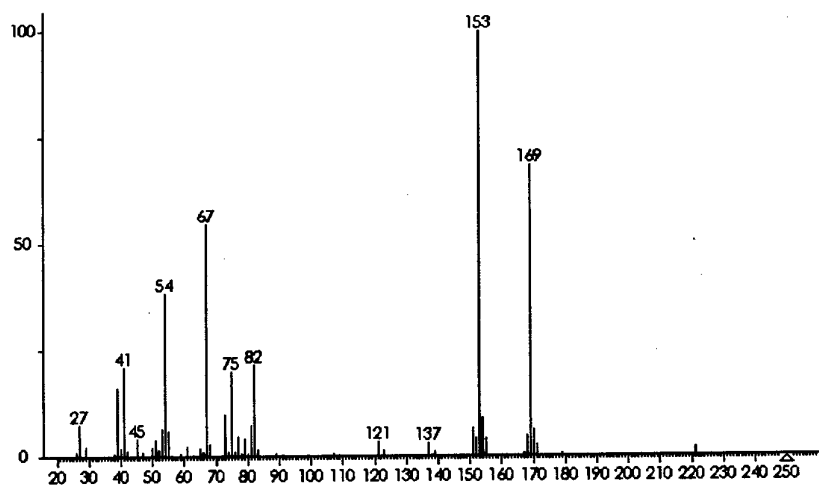


Figure A.22: Cyclohexyl trimethylsilyl methylphosphonate (MW 250).

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| 15. SUMMARY (MAXIMUM 200 WORDS (1044 BYTE)) The development of a procedure for the recording of reference mass spectra of trimethylsilyl (TMS) esters of alkyl and cycloalkyl methylphosphonates is described. The compounds are prepared <i>in situ</i> , on a small scale, from methylphosphonic difluoride and a selected alcohol dissolved in acetonitrile. Hydrolysis of the formed alkyl and cycloalkyl methylphosphonofluoridates to the corresponding methylphosphonates, evaporation to dryness and trimethylsilylation of the residue produces the TMS esters. The resultant reaction mixture is analysed by gas chromatography-mass spectrometry. In this way, electron impact mass spectra of TMS esters of 17 alkyl (ranging from butyl to nonyl) methylphosphonates and five cycloalkyl methylphosphonates were recorded. The mass spectra and a short description of the fragmentation processes of the TMS esters are presented. | | |
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